NGOTP Upstream Environmental Program
Modeling of Water Soluble Organic Content in Produced Water

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Statement of Problem:
Large amounts of brine are often associated with oil and gas production. Because these produced waters are in contact with oil at high pressures, they can become contaminated with water-soluble organic (WSO) compounds. The discharge of produced water in the Gulf of Mexico is regulated by NPDES permits, which specify that total oil and grease in the water be below a daily maximum of 42 ppm. Analysis of the produced water for total petroleum hydrocarbons by EPA methods 413.1 or 1664; however, does not distinguish between carboxylic acids and other polar compounds, and more environmentally harmful hydrocarbons. Hence, remediation of the billion barrels of produced water per annum is based on aqueous organic concentrations that may exceed the actual content of oil and grease. The goal of the project is to provide a computational tool, based on analysis and modeling of oil/brine samples, to be used to predict the water-soluble organic content in brines associated with deep well oil production. Such a model could be used prior to production from new facilities to assist in the development of a more selective and focused approach to produced water clean up, leading to cost savings and reduced environmental impact.

Comparison of New Technology to Existing Technologies
Algorithms for chemical thermodynamic modeling are commonly used in industry for a variety of systems. In particular, programs such as EQ3 are used to calculate the chemistry of groundwater systems that may be associated with oil and gas deposits. Hence, the challenge in developing a model of water-soluble organic behavior is not associated with the mathematics, but with the description of the chemical system under investigation. Complex modeling methods only generate reasonable answers if the system being described is already well known. The goal of this project is to develop a predictive tool for the solubility of general classes of organic compounds in brine, based on a few key input variables, such as pH, temperature and pressure.

Application and Benefits to Industry
Industrial partners will use the model to predict the production of water-soluble organics as a function of measurable parameters such as crude composition, formation characteristics, and produced water composition. This will enable the petroleum industry to identify aspects of produced water treatment that can be optimized to remove specific chemical classes of water-soluble contaminants. Such information can be used in the design of efficient and cost-effective water-treatment options for the next generation of offshore platforms for deep-water wells.

Tasks and Contributions of Research Team
This project supports the Petroleum Environmental Research Forum (PERF) project 98-04 "Managing Water Soluble Organics in Produced Water" by the development of a model for the solubility of organic compounds in produced water. Model development, carried out at ORNL, is progressing in stages to allow feedback from initial efforts to guide future emphasis. Industrial partners will provide analytical data on deep-water crude oil, produced water, and associated formation characteristics. They will guide the development of the model, then compare calculations with data from crude oil wells, and help to evaluate the data and model results for trends. All partners will be solicited for input on decisions relating to the direction of model development.

The proposed tasks in the development of a predictive model are given below.
1. Empirical analysis of 98-04 PERF data on water-soluble organics in simulated produced water.
The modeling effort began with an empirical analysis to quantify the effect of parameters such as pH and temperature on organic solubility in the aqueous phase. An uncertainty analysis of the water characterization carried out at ORNL showed that there was too much scatter for the data to provide the basis for an empirical model.

2. Development of a thermodynamic equilibrium model for PERF water characterization data
The crude oil-brine system was modeled based on the assumption of chemical thermodynamic equilibrium. The advantage of a thermodynamic equilibrium description is that variables such as temperature and salinity can be incorporated into the expressions for the activity coefficients. Volatile components can be modeled with an equation of state, which gives the dependence of solubility on pressure. The difficulty of formulating the model is in the selection of which components will

represent the system. NRTL activity coefficients were used successfully to fit laboratory data; however, it is difficult to extend this description to a multi-component system. Hence, the model was reformulated with a UNIFAC approach, where the properties of compounds, e.g., carboxylic acids or phenols, are dependent on activity coefficients derived from empirical correlations related to molecular size and the presence of functional groups.

3. Application of the liquid-liquid thermodynamic model to the calculation of organic solubility in oil/brine systems. The thermodynamic model was tested against the results of PERF 98-04 analyses to determine if the model would reproduce trends observed in the laboratory with the controlling factors (i.e., pH, temperature). The agreement between the model and the experiments was good. The work has been documented and has been submitted for publication in Chemosphere.

4. Compilation of international data. Results from the analyses of produced water from both the Gulf of Mexico and the North Sea will be compiled and assembled into a common format. Information has been collected from published (e.g., T.I. Utvik, Chemosphere, 39, 2593, 1999) and unpublished sources (e.g., Neff and Stout, 1999). This task will continue through the final year of the project.

4. Extension of model to account for oil field derived parameters. The final stage of model development will be to extend the produced water model to include field parameters, such as those related to drill-stem testing or methods of production. This step will involve discussion and cooperation with the petroleum industry to select the most relevant fitting parameters. A multivariate statistical analysis will be used – most likely a partial least squares methodology, which provides a number of advantages over other approaches. Simplifying assumptions are not required, and the analysis should be able to identify the most important factors controlling organic solubility in produced water. Data requirements are not restrictive. Hence, a wide range of brine/oil systems can be included in the analysis, as long as similar data are available for each system. Qualitative as well as quantitative variables can be included in the model, such as geographic location, geochemical characteristics such as sulfur content, and the chemistry and origin of the produced water. Such variables, along with laboratory- or field-based measurements of temperature, pressure and pH, will increase the breadth of a statistical comparison. Some of the data will be selected for model development, and a separate group for model validation. One objective of the statistical analysis will be to identify the most important variables that govern organic solubility in produced water from existing oil fields, and to be able to extend the analysis to new oil fields. Industrial partners will be invited to provide data for the analysis, and to give feedback on model successes and areas requiring improvement, and on documentation of project achievements.

Deliverables

FY2003

- Database of thermodynamic parameters associated with water-soluble organic compounds for use in thermodynamic model.
- Compilation of organic solubility data from literature and industry sources from a variety of oil fields.
- Test of predictions of the thermodynamic model against available data.

FY2004

- Statistical model to predict solubility in new oil fields, or under changed environmental conditions.

Why DOE funding is required:

The produced-water waste stream is of concern to all oil producers, large companies as well as the smaller independent producer. Off shore and on-shore facilities alike will benefit from a general predictive model of water-soluble organic contamination of produced water, which will assist in the development of cleanup methods that are efficient and cost-effective. The government has a role in assisting all producers to comply with environmental regulations, and to ensure a diverse and secure energy supply.

Critical Decision Points

The decisions in this project relate to the best approach to model development. A number of methods (i.e., empirical, phenomenological, statistical) can be applied to describe the oil/brine system. An important goal of this project is to derive selection criteria for a predictive model based on one (or more than one) of these methods.

September 2002: The ORNL characterization data were used to test the thermodynamic model. They can also be used as part of the "training" data set for a statistical model. However, they are inappropriate for lumped parameters or for the basis of a robust empirical model.

May 2003: A thermodynamic equilibrium activity coefficient model reproduced trends in solubilities measured in ONRL characterization experiments and published sources.

September 2003: The partial least squares method was selected to incorporate field-based parameters into a predictive model.

Accomplishments in FY2003

The type and amount of organic chemicals that are soluble in produced water associated with deep-well oil production are not well understood, leading to inefficiencies in produced water cleanup prior to its discharge into the ocean. Hence, industrial partners (ChevronTexaco, Conoco-Phillips, Shell, and Statoil) and ORNL have embarked on a study of organic solubility in produced water, including the characterization and modeling of the organic component in produced water. A project that characterized simulated produced water in contact with actual samples of crude oil was performed at ORNL between 1999 and 2002. The focus of the modeling project in its first year, FY2002, was to evaluate these characterization data for model development and to describe trends in the data using simple univariate correlations. The empirical approach was not successful because of the uncertainties in the experimental results, and so a liquid-liquid equilibrium model was developed to reproduce the trends seen in the characterization data, specifically the increase in solubility with pH. The model was formulated based on the assumption of chemical equilibrium, with the hydrocarbon and aqueous liquid phases described using activity coefficients from non-random two-liquid (NRTL) and UNIFAC calculations. The chemical thermodynamic model was further refined during FY2003, and eventually included data for 21 different compounds, representative of produced water contaminants (alkanes, organic acids, alcohols, aromatics, polyaromatic hydrocarbons and esters). To account for the uncertainties in the initial concentrations, these concentrations were converted into normal distributions that were randomly sampled for input into the thermodynamic calculation. The results from these calculations reproduced the trends observed in the laboratory, and have been submitted for publication to Chemosphere.

Although the application of a thermodynamic model to the produced water system was successful, it became apparent that there would be difficulties in developing a predictive algorithm for the crude-brine system based on published produced-water data. A thermodynamic model requires detailed knowledge of the chemistry and physics of the system of interest, so that chemical parameters specific to each of the contaminants can be included in the computation, such as activity coefficients. This degree of detail does not exist for most of the data sets on Gulf of Mexico crude, and indeed will not be available for new and aging wells. Hence, a different approach to modeling is now being considered, using chemometric analysis instead of detailed thermodynamic calculations. The chemometric, or statistical approach, readily allows field data to be incorporated into the model - information that can be gathered *in situ* (on an oil platform). The model is based on published data that covers a wide range of conditions, encompassing those that would be encountered in the system for which predictions are to be made. A partial least squares analysis was performed on the ORNL characterization data, generating a correlation for predicting solubilities over the range of physical conditions varied in the experiments. The next step will be to develop a model based on a wider set of data, to cover conditions that are encountered in deep-ocean drilling. Hence, to this end, international data on produced water contamination was surveyed: including information from the Gulf of Mexico, the North Sea, and on-shore gas wells.

The ultimate goal of the project is to assist the petroleum industry target produced water cleanup to best protect the environment. The first two years of the project have been focused on understanding the physical and chemical phenomena that govern organic solubility in produced water under a variety of conditions. The goal of the final year of the project will be to bring this information together in a predictive model for use in new oil fields, or under changing environmental conditions.

Publications & Presentations

J. McFarlane, D.T. Bostick, H. Luo. 2002. "Characterization and Modeling of Produced Water", in Proceedings of the Ground Water Protection Council Produced Water Conference, Colorado Springs, CO, Oct. 16, 2002.
J. McFarlane, D.T. Bostick, H. Luo, "Analysis and Modeling of Hydrocarbon Contamination in Produced Water", submitted to Chemosphere.
J. McFarlane, "Application of Chemometrics to Modeling Produced Water Contamination", Separations Science and Technology, in press.
J. McFarlane, D.T. Bostick, H. Luo, "Characterization and Modeling of Produced Water Contacted with Gulf of Mexico Crude Oil", Presented at the Ground Water Protection Council Produced Water Conference, Colorado Springs, CO, Oct. 16, 2002.
J. McFarlane, D.T. Bostick, H. Luo, "Characterization and Modeling of Produced Water Contacted with Gulf of Mexico Crude Oil", Presented at the Southeast Regional Meeting of the American Chemical Society, Charleston, SC, Nov.14, 2002.
J. McFarlane, University of Tennessee Chemical Engineering Department, Knoxville, TN, Sept. 23, 2003.
J. McFarlane, "Gulf of Mexico Produced Water: Characterization and Simulation", American Association of Petroleum Geologists Mid-continent Meeting, Tulsa, OK, Oct. 14, 2003.
J. McFarlane, "Gulf of Mexico Produced Water. Characterization and Simulation", 13th Separations Science and Technology Conference, Gatlinburg, TN, Oct. 27, 2003.